



10th International Conference Solid State Chemistry, Pardubice, Czech Republic

Arrhenian and Non-Arrhenian temperature dependent relaxation time development in the solid-liquid transition area of amorphous bodies

Bořivoj Hlaváček^{a*}, Čestmír Drašar^b, Andréa Kalendová^a, Pavel Menc^a,
David Veselý^a

^a*Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

^b*Department of Applied Physics and Mathematics, Faculty of Chemical Technology, University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic*

Abstract

The temperature-dependent changes of molecular and sub-molecular motions are studied in amorphous substances. The solid and liquid phases of amorphous bodies are characterized at the micro-level by two types of oscillators, linear and non-linear. It is accepted that an amorphous liquid is formed by domains that group the linear oscillators into the form of icebergs. The serial connection of the viscoelastic elements are arranged inside of these icebergs. The size of the linear connection within the domains is characterized by the number “n”, which increases during the cooling process. The linear viscoelastic behavior of the individual serial connections is connected to the individual relaxation processes α , β , and γ . Only the “alpha” process exhibits growth of “n” to infinity on cooling. Therefore, the corresponding relaxation time, τ_α , for the infinite chain of “n” elements (Voigt or Maxwell elements) can also reach infinity as the material transforms to a glassy state. In contrast to the “alpha” process, the β and γ processes are limited in growth for serial connections in a chain structure. Therefore, the relaxation times for the β and γ processes, τ_β and τ_γ , will only follow the temperature dependence of the sample viscosity on cooling, which is, of course, Arrhenian. We discuss the role of non-linear oscillators in the solid-liquid transition in relation to Brownian motion.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).

Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.

Keywords: Solid-liquid transition, relaxation processes α , β , γ , deterministic chaos, molecular vibrations, Brownian motion.

* Corresponding author. Tel.: +420-466-037-192.

E-mail address: borivoj.hlavacek@upce.cz.

1. Introduction

In the model presented below, the solid and liquid phases of amorphous bodies are characterized at the micro-level by two types of oscillators, which are associated with two different types of theories [1]: 1. the deterministic chaos theory [1,2] and 2. the linear viscoelasticity theory [3]. It is accepted that an amorphous liquid is formed by domains [4,5] that group linear oscillators into the form of icebergs that contain the viscoelastic elements arranged in a serial connection [3,6]. The size of the linear chain within the domains is characterized by “n” number of elements that increase during the cooling process. The linear viscoelastic behavior of individual serial chains is associated with the individual relaxation processes α , β , and γ [7-11]. Only the “alpha” process exhibits growth of “n” to infinity upon cooling [8-11, Fig. 7]. Therefore, the corresponding relaxation time, τ_α , for the infinite chain of elements (Voigt or Maxwell elements) can also reach infinity as the material transforms into a glassy state. In contrast to the “alpha” process, the β and γ processes are limited in growth for serial chaining; i.e., these processes are limited in the number of “n” elements. Therefore, the relaxation times for the β and γ processes, τ_β and τ_γ , will only follow the temperature dependence of the sample viscosity on cooling, which is, of course, Arrhenian. The relaxation times, τ_β and τ_γ , exhibit a linear dependence in the reverse temperature scale, which is similar to the dependence of η/T , [8-11]. When transitioning from the glassy state to the liquid state (through processes of temperature growth), the individual icebergs will release non-linear oscillators (N.O.) (Fig. 2) in the form of standalone molecules or fragments, which are then subdued by the motion of chaotic oscillators and are the primary contributors to the optically visible trembling character of Brownian motion. The non-linear oscillators are the primary source of uncertainty in particle trajectories. Therefore, if we change the warming process of the sample back to a cooling one, the N.O. will reattach to the icebergs quite irregularly. Therefore, we must consider that the consequent glassy state is always amorphous and chaotic upon formation. Thus, from the thermodynamic point of view, the glassy state represents a lawfully positional disorganized state and a state that we cannot identify from the potential minima of the Helmholtz-Gibbs energy.

2. The visual representation of the solid state model

The specific heat model of the solid state [12-16]

- Model of a perfect crystal with no thermal motion
- Symbols “ u_n ” represent the displacement of the particles from the potential minima
- Density of vibrational states, $\rho(\omega)$, as a function of frequency, ω

Equation of motion

$$m \cdot \frac{d^2 u_n}{dt^2} = \beta \cdot [(u_{n+1} + u_{n-1}) - 2u_n]$$

$$\tau_n = \frac{\tau_{\max}}{n^2}$$

$$3N = \int_0^{\omega_{\max}} dZ = \int_0^{\omega_{\max}} \sigma(\omega) d\omega$$

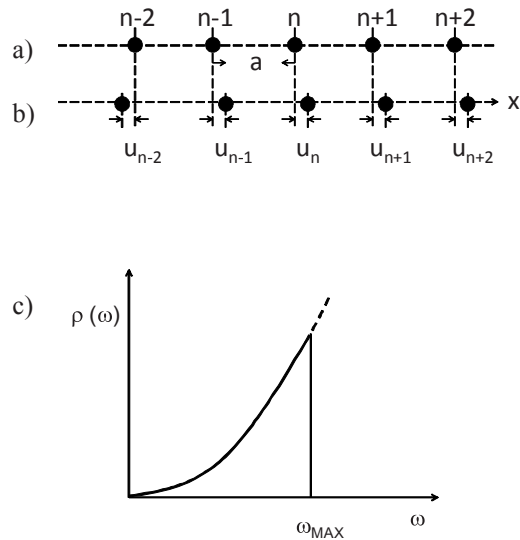


Fig. 1. The model of a finite series of linear oscillators as a representation of the solid state. Individual atoms serve as the vibrating points that carry only vibrational energy.

3. Graphical illustration of the onset of the softening point

The softening point is characterized by the first appearance of N.O. This phenomenon usually appears in the vicinity of the T_g of the amorphous bodies.

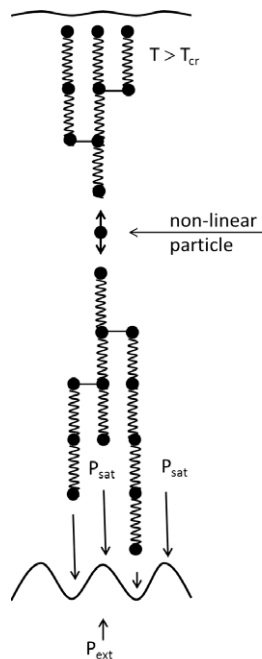
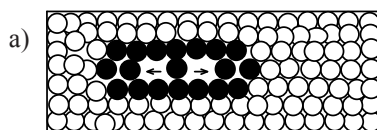


Fig. 2. Graphical illustration for the interaction of the non-linear oscillator with other linear oscillators in its vicinity; the void space created by the N.O. is unable to carry a shear module, and thus the solid amorphous sample begins its slow-paced change to a liquid state as the temperature increases.

4. Consequences for the appearance of non-linear oscillators in a solid body

a) Visual representation of the “push-aside” effect of a non-linear oscillator. The non-linear oscillator switch pushes aside the linear oscillators in its vicinity.



b) The amplitude switch of a non-linear oscillator that demonstrates the “need for space”.

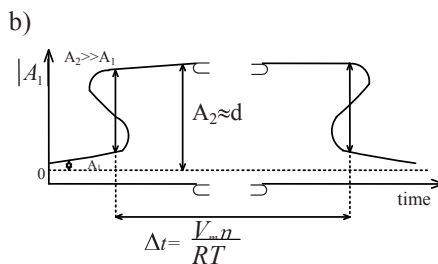


Fig. 3. Graphical illustration of the discontinuity in the amplitude of the vibrations of a non-linear oscillator . As a result of the appearance of this “new species” (above the T_g temperature), the overall volume of the sample also changes. After this point, the physical properties exhibit a stronger dependence on temperature compared to the glassy state. Above the T_g , the discrete energy levels of the partition function become increasingly separated compared to the glassy state. To explain the decrease in the specific heat of the sample with decreasing temperature, A. Einstein [14] and P.J.W. Debye [15] also had to introduce the concept of discrete energy levels for the harmonical oscillator. Because the energies of a harmonical oscillator are quantized, the amplitudes of discrete vibrations must also have discrete forms.

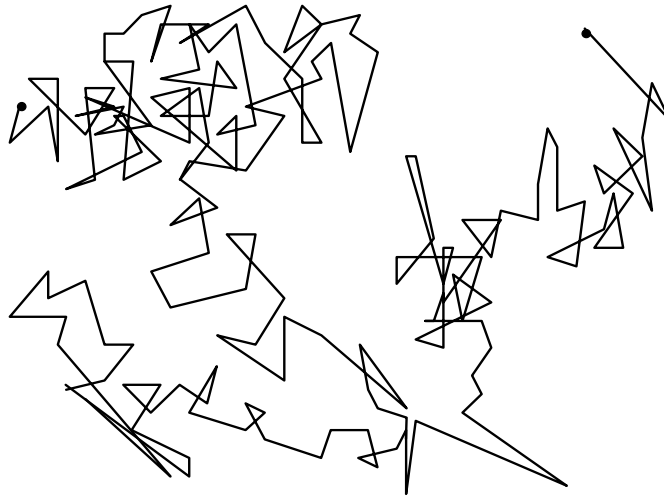


Fig. 4. A basic picture of the travel path of a particle through the liquid matrix, which shows the nature of a random walk. In reality, the straight lines on the picture are simplifications that ignore the “trepidation” character of each prime line at the micro-level, which are followed and observed in a much shorter time interval. (For more details, see R. Brown, Edinburgh New. Phil. J. 5, 358, (1828). **In our view, “trepidation” is a manifestation of the switches in amplitude of non-linear oscillators.**

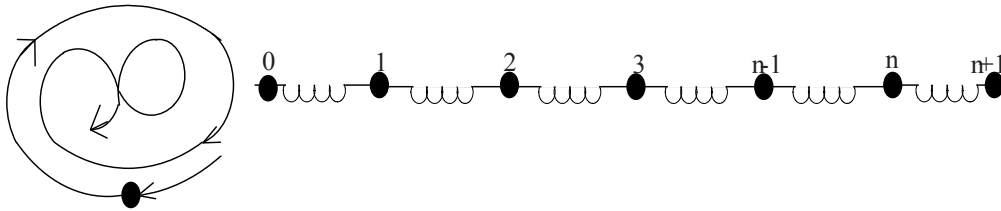


Fig. 5. Schematic illustration of the N.O. in serial combination with a chain of linear oscillators (L.O.). The N.O. is a carrier of non-deterministic features [1,2]. The series of L.O. has a classical mathematical solution that provides the series of relaxation times, τ . The length of the linear chain within the domains is characterized by the number “ n ”, which increases with decreasing temperature due to the disappearance of the non-linear oscillators. With an increasing number of interconnected “ n ”, which increases upon cooling, the domain size also increases. This process is illustrated in Fig. 6, below.

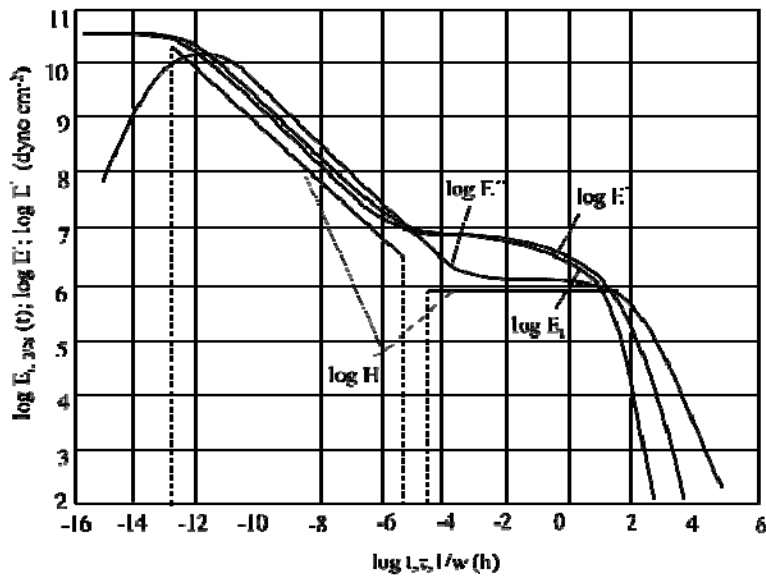


Fig. 6. How the increasing number of “n” elements in a chain influences the basic forms of a linear viscoelastic material behavior in the primary transition zone for the polymer poly-isobutylene. Characteristic data were reported as standard data by A.V. Tobolsky [17]. We observe wedge-like relaxation spectra. The range of relaxation times in the primary transition zone (from τ_{\max} to τ_{\min}) is determined by the number of “n” elements in the domains, i.e., by the size of the icebergs. The box-like spectra reveal the extent of domain–domain interconnections for a rubber-like state. The size of the box-like spectrum corresponds to the level of external interconnections of domains, which, in special cases, can be interpreted as the mutual macromolecular entanglements. We can provide the calculated number of linear elements based on the general definition of the relaxation time of a sample; this number can be calculated from the measured functions of the relaxation moduli, $G(t, T)$ or real $G'(\omega, T)$, and the imaginary parts of the dynamical moduli, $G''(\omega, T)$ [3,18-20].

The general definition of the relaxation time is [18-20]

$$\Theta_{\text{int}, 1} = \frac{G(t, T)}{d G(t, T) / dt}$$

$$\Theta_{\text{int}, 2} = \frac{G'(\omega, T)}{G''(\omega, T) \omega}$$

This calculation is performed based upon the experimental data provided by A. V. Tobolsky for a wedge-like spectrum [17].

$$\tau_{\max} = 10^{12.5} \text{ hours} = 3.6 \cdot 10^{9.5} \text{ sec}$$

$$\tau_{\min} = 10^{-5.4} \text{ hours} = 3.6 \cdot 10^{-2.4} \text{ sec}$$

The Rouse linear model [6] provides us with the expression in discrete time

$$\tau_{\max} = n^2 \cdot \tau_{\min}$$

However, we obtain a number for n that is too high ($n > 3000$) and that contradicts the results from viscosity and other rheological measurements [3, 21], which indicates an abrupt change in the physical properties of polymers for a substantially smaller number of

elements, $n \approx 660$ [3,21]. This number can be obtained using the more general form of the Carreau-Bird non-linear model [22-24], where the exponent α for the separation of relaxation times is adjustable

$$\tau_{\max} = n^{2\alpha} \cdot \tau_{\min}$$

Thus, this model allows all of the rheological properties to be predicted [21] by taking the number of elements to be $n=660$. This interesting number indicates a cross-over from a domain area into a liquid form:

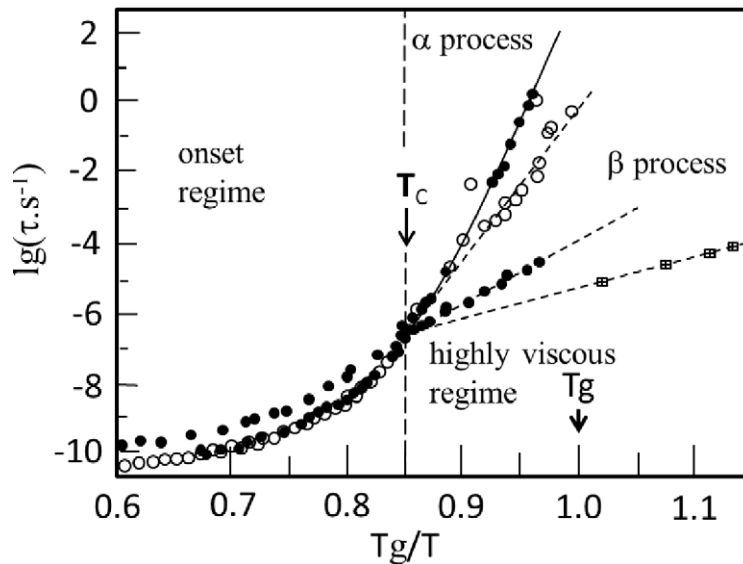


Fig. 7. The experimental data of the integral relaxation time according to Rossler [10], Surovtsev [8,9], Wiederich [11], and colleagues, which reflect the Arrhenian and Non-Arrhenian temperature dependencies. This figure is presented to provide a better explanation of the α , β , and γ relaxation processes based upon the serial interconnections of the viscoelastic elements (shown in Fig. 5 and Fig. 6) and presented in framework of the P.J.Carreau – R.B. Bird series [22-24].

Conclusions

The results from the vibrational model of the glass-liquid transition have provided us with a very precise picture of the glassy liquid transition using the models of linear and non-linear oscillators.

- Non-linear oscillators are the primary source of uncertainty in the trajectories of the particles. Therefore, if we change the warming process of the sample back to a cooling run, the N.O. will attach to the icebergs quite irregularly. Therefore, we suggest that the subsequent glassy state is **always amorphous** and chaotic at its origin. From a thermodynamic perspective, the glassy state represents a lawfully positional disorganized state and a state that we cannot identify with the potential minima of the Helmholtz-Gibbs energy.
- The relaxation spectra of the primary transition zone reflect the connections of viscoelastic elements inside heterogeneous domains. The box-like spectrum in Fig. 6 reflects the serial external domains interconnection, which are designated as “entanglements” in polymer rheology [3].
- The limited number of linear elements arranged in a series (See Fig. 5) on cooling is the primary reason for the Arrhenian behavior of the sample relaxation time dependence for the β and γ relaxation processes.
We assume that the number of viscoelastic components in the series of linear elements is constant for the β and γ processes. The opposite behavior holds for the α process, in which the inter-connection of linear elements may increase to infinity during sample cooling.

References

- [1] H.J. Pain., "The Physics of Vibration and Waves" J. Wiley, London, New York (1997), ISBN 047193782 8 (pbk)
- [2] M. Marek and I. Schreiber, "Chaotic Behavior of Deterministic Systems" Academia Praha, Publish in co-edition with Cambridge University Press, Great Britain, (1991), ISBN 80-200-0186-7.
- [3] J.D. Ferry "Viscoelastic Properties of Polymers" J. Wiley, New York (1961).
- [4] G. Tammann, "Die Aggregatzustände", Leipzig: Leopold Voss Verlag; (1922)
- [5] Porai-Koshitz E A, "Structure of Glass" Proceedings of the 4th, All-Union Conference on the Glassy State, Leningrad (1964).
- [6] P. Rouse, J. Chem. Phys. 21, 1272 (1953).
- [7] F. Bueche "Physical Properties of Polymers" pp.258,285, Interscience Publishers (1962).
- [8] N.V. Surovcev, S.V. Adichchtev, E.Rossler and M.A. Ramos, J. Phys.: Condens. Matter 16, 223, (2004).
- [9] N.V. Surovcev, J. Wiederich, A.E. Batalov, V. N. Novikov, M.A. Ramos, E. Rossler, J. Chem. Phys. 113, (4) 5891 (2000).
- [10] E. Rossler and P. Eiermann, J. Chem. Phys, 100 (1994) 5237.
- [11] J. Wiedersich, N. V. Surovtsev, and E. Rossler, J. Chem. Phys. 113, 1143- 1153 (2000).
- [12] Ch. Kittel, Introduction to Solid State Physics 3rd. Ed. New York, London: Wiley; (1996), p.184
- [13] J. Frenkel, Kinetic Theory of Liquids. New York: Dover Publ; (1959).
- [14] A. Einstein: Ann.Physik, 22 (1906), 180, 800, 34 (1911), 170.
- [15] P.J.W. Debye "Topics in Chemical Physics" Elsevier, Amsterdam / New York 1962.
- [16] B. Wunderlich in E.A. Turi, Thermal Characterisation of Polymers, Vol. 1 Academic Press, New York, (1997)
- [17] A.V. Tobolsky, "The Properties and Structure of Polymers" J. Wiley, New York (1960).
- [18] B. Hlaváček, J.F. Stanislav, and F.A. Seyer, "Stress Relaxation of Viscoelastic Material" Transactions of Soc. Rheol. 18: 1, 27 – 44, 9 (1974).
- [19] B. Hlaváček and F.A. Seyer, J. Appl. Sci. 18, pp 423 – 439, (1972)
- [20] B. Hlaváček and P.J. Carreau, "Correlation Between Linear and Non-linear Viscoelastic Data for Polymer Solution, in Theoretical Rheology", ed. By J.F. Hutton, J. R. A. Pearson and K. Walters, Appl. Sci. Publishers, London, (1975).
- [21] S. Middleman " The Flow of High Polymers " pp. 169, Intersciences Publishers, New York, London, (1969).
- [22] P.J. Carreau, Trans. Soc. Rheol. 16(1), 99 (1972).
- [23] P.J. Carreau, I. F. MacDonald, R. B. Bird, Chem. Eng. Sci., 23, 901, (1968).
- [24] R.B. Bird, P. J. Carreau, Chem. Eng. Sci., 23, 427, (1968).